WAVELENGTH DISPERSIVE X-RAY FLUORESCENCE SPECTROMETRY AS A TOOL TO STUDY THE EFFECTS OF PYRIDINE ON THE INORGANIC MOIETIES IN THE ARGONNE PREMIUM COALS.

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INTRODUCTION. Several manuscripts have appeared within the time frame of the Argonne Premium Coals Sample Program which have addressed the inorganic moieties contained in these coals. At the same time, numerous studies of the effects of liquids on the micro- and macro-level structuring in coals have been undertaken. This group, using x-ray diffraction, helped define the crystalline moieties in the APC's and, using x-ray scattering methods, has been studying the effect(s) of the additions of liquids on the average inter-layer distance for several of the coals. For many of these studies (including ours), pyridine has been of the liquids receiving primary focus - perhaps because of its polarity and its ability to form hydrogen-bonds. In addition, its aromaticity (and thus planarity) offers other possibilities for interactions with the organic moieties in coals. However, these same structural features cause pyridine to be an effective ligand towards metal ions – particularly the soft metal cations found in coals; and a extensive coordination chemistry exists using pyridine as either the solvent, and an inner-coordination sphere ligand, or both. In addition, pyridine has the capability to interact with both "inorganic" and "organic" sulfur. Consequently, the abundances of important inorganic species such as FeS_2 may be effected by the presence of excess pyridine. Presented below are the first results of a study of the gels produced by reacting pyridine with the APC's.

Experimental. 25 Mls of anhydrous pyridine (Aldrich) were added to a 5 grams (-100 mesh) sample of each of the Argonne Premium Coals. Each sample was allowed to equilibrate for 10-14 days. At the end of this period, the gels formed from the coal-pyridine interactions was separated from the remaining liquid by filtration. Each gel was air-dried and then mounted onto a sampleholder. A wavelength dispersive x-ray fluorescence (WDXRF) spectrum was obtained by irradiating each gel with rhodium Xrays (from an end-centered x-ray tube). The secondary Xrays emitted by each gel were focussed onto a graphite monochromator (d = 3.342 Å). The WDXRF spectrum was obtained by accumulating intensity data for 4 seconds at angular increments of $\Delta 2\theta = 0.05°$ over the angular range from $2\theta = 8.00°$ to 140.00°. In terms of the wavelength and the energy of the secondary Xrays, this angular region corresponds to:

2θ	λ	ϵ
8.00°	0.47 Å	26.4 keV
140.00°	6.30 Å	1.97 keV

For comparison purposes the WDXRF spectrum of each of the APC's was also obtained.

RESULTS. Shown in Figure 1 are the superimposed WDXRF spectra of the eight Argonne Premium Coals. These spectra indicate the advantages of the wavelength dispersive method, good peak resolution and good signal/noise ratio. These spectra indicate that the eight APC's contain many of the same inorganic atoms, but in considerably different proportions. Principal among these are iron, calcium, and sulfur – which represent the major components. In addition, small peaks due to either titanium and/or potassium also appear in at least two of the spectra. These spectra verify the existence of the inorganic moieties previously reported.

The intensity of a specific peak in the WDXRF spectrum of a sample containing many components may be written as:

$$I_A(\lambda_A) = \eta_A \cdot M(\lambda_A) \cdot I^*_A(\lambda_A) \cdot \exp(-t_S \cdot \{\rho_S \cdot [\mu_S(\lambda_{Rh}) + \mu_A(\lambda_A)]\}). \quad (1)$$

In eq 1, $I_A(\lambda_A)$ is the intensity, typically in counts or counts per second, measured in the WDXRF spectrum and due to ana abundance of η_A of analyte A in the sample S. The efficiency of the spectrometer for detecting Xrays at wavelength λ_A is given by M. $I^*_A(\lambda_A)$ is the absorption and enhancement-corrected intensity due to 100% analyte A and may frequently be determined by iterative methods. The exponential includes several factors and is typically referred to as the matrix absorption effect(s). Among these factors are the mass absorption coefficients of the sample for the incident Rh Xrays and the mass absorption coefficient for the secondary Xrays produced by analyte A, the density of the sample (ρ_S) and the thickness of the sample (t_S). Using mixtures of model compounds, the product of M•I* is being determined for a number of the important analytes in these coals. In addition, the sample thickness is controlled by the opening in the sampleholder. Consequently, for comparisons, several of the parameters noted in eq 1 may be eliminated from further considerations.

Shown below is the WDXRF spectrum of an Argonne Premium coal compared to the WDXRF spectrum of the gel formed when that coal has been treated with pyridine. A summary of the analysis of the intensity under the iron K_α peak, the calcium K_α peak, and the sulfur K_α peak is presented in Table I.

TABLE I. COMPARISON OF PEAK INTENSITIES.

COAL	PEAK INTENSITIES IN COUNTS PER SECOND					
	Fe PEAK @ 1.94 Å		Ca PEAK @ 3.36 Å		S PEAK @ 5.37 Å	
	Coal	Gel	Coal	Gel	Coal	Gel
APC 101	19,083	15,007 -21%	2,181	1,822 -16%	2,005	1,734 -14%
APC 301	33,594	28,227 -16%	4,790	4,302 -10%	5,785	4,553 -21%
APC 401	16,008	10,451 -35%	2,026	1,388 -31%	4,089	2,621 -36%

Comparison show that the peaks intensities for these inorganics parallel their previously reported abundances, verifying the accuracies of the WDXRF method used in these experiments -- at least at a semi-quantitative level.

Peak intensity comparisons also show that in the transformation from the coal to the gel, the intensity of each peak is reduced -- by approximately the same amount. Each intensity reduction indicates that the abundance of each of these key inorganic moieties is also decreased. However, the cause(s) of the reductions in peak intensities has not been established unequivocally. This uncertainty in interpretation of the WDXRF spectra is because of the versatility of pyridine in its reaction(s) with coal. Specifically, it is known that pyridine causes coals to swell, which at the molecular level, is consistent with a change in the density of a powdered sample. The inclusion of pyridine into the organic matrix of the coal to form the gel causes a reduction in the abundances of the inorganic moieties in the coal. Both the change in abundances and the density change will affect the intensity of the analyte in an exponential manner. In addition, pyridine may complex with one (or more) of the inorganic analytes in the coal in such a manner as to be removed from the gel which is formed upon pyridine addition, thus causing a reduction in the abundance of that analyte.

Figure 1. WDXRF spectra of the Argonne Premium Coals.

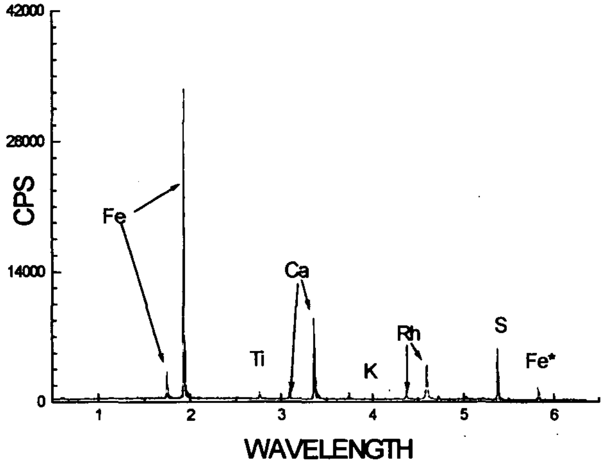

Figure 2. WDXRF spectra of APC 101 and its gel formed with pyridine.

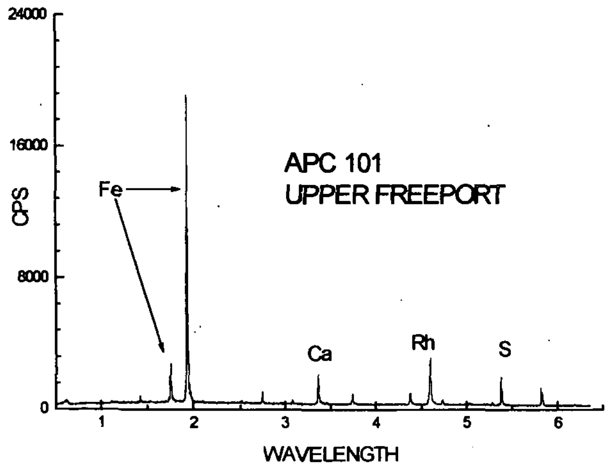

Figure 3. WDXRF spectra of APC 301 and its gel formed with pyridine.

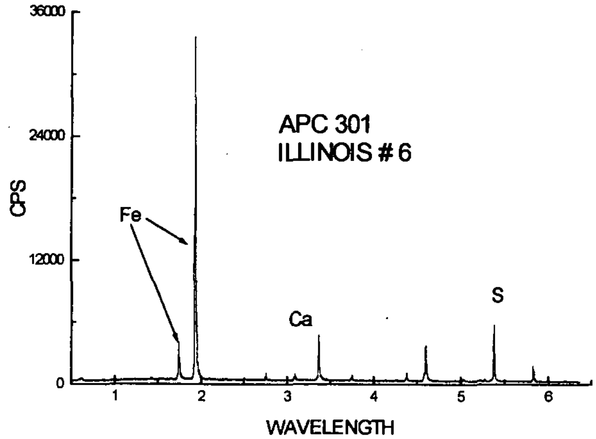

Figure 4. WDXRF spectra of APC 401 and its gel formed with pyridine.